Limiting Viscosity Number-Molecular Weight Relationship of Cellulose in N-Methylmorpholine-N-oxide

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N-メチルモルホリン-N-オキシド中における セルロースの極限粘度数と分子量の関係

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Résumé

A limiting viscosity number—molecular weight relationship for cellulose in N-methylmorpholine-N-oxide at 80°C has been established in the form of Houwink-Mark-Sakurada's equation. The cellulose samples having a wide range of molecular weight by an acid hydrolysis were acetylated, followed by the fractionation of the cellulose triacetate in methylene chloride—ethyl alcohol system, and the weight average molecular weight of each fraction was evaluated by the sedimentation equilibrium method at 25°C in acetone. Each fraction was deacetylated, and the limiting viscosity number of the regenerated cellulose was determined in N-methylmorpholine-N-oxide monohydrate solvent at 80°C. The relationship between the limiting viscosity number, in cm^3g^{-1}, and the weight average molecular weight, in g mol^{-1}, was found to be $[\eta]=0.087\ \bar{M}_w^{0.66}$.

要　　旨

非水系セルロース溶媒であるN-メチルモルホリン-N-オキシド中において，80°Cにおけるセルロースの極限粘度数と重量平均分子量の関係を求めた。広い範囲の分子量を持つセルロース試料を得るために，木綿を酸加水分解した。加水分解したセルロースをアセチル化した後，セルロースアセテートを塩化メチレン—エチルアルコールで分別沈殿法により分別した。分別された各セルロースフラクションの分子量を，アセトン中で25°Cにおいて沈降平衡法により測定した。一方セルロースアセテートの各フラクションを脱アセチル化し，再生されたセルロースの極限粘度をN-メチルモルホリン-N-オキシド中において，80°Cで測定した。極限粘度数と重量平均分子量の両対数プロットより，Houwink-Mark-桜田の式の定数として以下の値が求められた。

$$[\eta]=0.087\bar{M}_w^{0.66}$$

(80°C，N-メチルモルホリン-N-オキシド中)

ここで，$[\eta]$：極限粘度数，ml g^{-1}

$\bar{M}_w$: 重量平均分子量, g mol^{-1}

1. Introduction

Over the past ten years there has been an increased interest in new organic solvents for cellulose. They are cyclic amine oxides[1], dimethyl sulfoxide—paraformaldehyde[2,3], dimethyl sulfoxide—amine[4], dimethyl formamide—nitrogen tetraoxide mixtures[5].

Among the various new organic solvents N-methylmorpholine-N-oxide (MMNO), a cyclic amine oxide, stands out because of its unusual properties. MMNO is a crystalline monohydrate at room temperature and melts at 72°C. When heated to around 100°C, MMNO is able to dissolve readily several percent of high molecular weight cellulose. Even though the mechanism of dissolution is not understood, it has been shown by nuclear magnetic resonance spectroscopy that this cellulose solvent is neither derivatized nor complexed[6]. In that sense MMNO differs from other organic solvent mixtures in which cellulose is converted into labile derivatives. Therefore, only in the case of cyclic amine oxides, one could speak of "true solution" of cellulose.

The purposes of the present investigation are to study the behavior of cellulose in this solvent, and to evaluate the constants for the limiting viscosity number—molecular weight relationship for this cellulose solvent.

2. Experimental

2. 1 Samples

The cellulose samples used in this stuby was the acid hydrolyzed residues of an absorbent cotton which had been previously used for an acid hydrolysis study[7]. The residues were further hydrolyzed with 6N HCl solution at 97°C for 60 min in order to obtain samples with widely distributed molecular weight.

2. 2 Acetylation of cellulose and fractionation of cellulose triacetate

The solubility of a cellulose acetate in a solvent—precipitant system depends to various extent on both its molecular weight and degree of substitution. Therefore, an acetylation reaction has to be chosen in which the solubility of cellulose acetate depends solely on its molecular weight. Thus the acetylation medium used in the present study was anhydrotrifluoroacetic acid—acetic acid—chloroform[8] in which the least degradation and the highest degree of substitution are expected. The degree of substitution of the cellulose acetate based on its nuclear magnetic spectrogram was 2.9, and the yield was 82.8%.

The cellulose triacetate (CTA) was fractionated at 25.00±0.04°C by making successive ethyl alcohol (precipitant) additions to a 1.0% solution in methylene chloride. In the fractionation process, as soon as a small amount of precipitate was noticed, the addition of ethyl alcohol was stopped. The precipitate was redissolved by raising temperature of the mixture to 38°C, and reprecipitated by slow cooling to 25.0°C in 24 hours. Thus a sharper molecular weight distribution would be expected for each fraction. Each precipitate was removed by centrifugation in a centrifuge at room temperature, and washed twice with

methyl alcohol and vacuum dried. The last fraction was collected after evaporation of the residual solution with a rotary evaporator.

All fourteen fractions were subjected to a gel permeation chromatographic analysis using a high pressure liquid chromatograph (Differential Refractomter R401, Model 401, Waters Co. Ltd.). Among fourteen fractions seven were chosen for further experiment based on their chromatograms. The results of the fractionation are given in Table 1.

2. 3 Molecular weight determination of cellulose triacetate

A weight average molecular weight of the CTA fractions were determined in acetone by the sedimentation equilibrium method using an ultracentrifuge (Beckman-Spinco type E). This method does not require independent measurement of the diffusion coefficient in order to fix the molecular weight, and is based on a condition of zero net flux across any plane in the solution normal to the radius of the cell[9]. At the top meniscus and at the bottom of the cell, there can never be any net flux, so that the equilibrium condition must fold at these sections at all times. Shortly after the centrifuge is brought its maximum speed, therefore, a determination of the concentrations at these planes can be used to give the equilibrium values. The concentrations were determined from Rayleigh interference diagrams.

The apparent molecular weight, $\overline{M}_{w\ app}$, is evaluated from the following equation

$$\overline{M}_{w\ app}=\frac{2RT}{(1-\bar{v}\rho)\omega^2(r_b^2-r_m^2)}\left(\frac{C_b-C_m}{C_o}\right) \qquad \cdots\cdots(1)$$

where R=gas constant, 8. 13 joule deg^{-1} $mole^{-1}$, T=experimental temperature, 298K, $\bar{v}$= specific volume of CTA, 0. 752cm^3g^{-1}, ρ=density of acetone, 0. 792g cm^{-3}, ω=angular velocity, rad sec^{-1}, r_m=distance between the center of the rotar and the top meniscus, r_b= distance between the center of the rotar and the bottom, C_m, C_b, and C_o=concentrations at the top meniscus, at the bottom, and initial concentration, respectively.

The weight average molecular weight is given by the following equation

$$\frac{1}{\overline{M}_{w\ app}}=\frac{1}{\overline{M}_w}+\left(B+\frac{\bar{v}}{\overline{M}_w}\right)\left(\frac{C_m+C_b}{2}\right) \qquad \cdots\cdots(2)$$

where B=the second virial coefficient. When the reciprocals of apparent molecular weight are plotted against $(C_b+C_m)/2$ for various concentrations, $\overline{M}_w$ can be evaluated by extrapolating $(C_b+C_m)/2$ to zero. Figure 1 shows typical plots of $1/M_{w\ app}$ against $(C_b+C_m)/2$ for three different concentrations, 0. 1, 0. 2 and 0. 4%, of the fraction IV.

2. 4 Deacetylation of cellulose triacetate

The fractionated cellulose triacetate was immersed into 2M sodium methoxide—methyl alcohol mixture, and kept overnight at 20°C. The sample thus deacetylated was thrown into a large excess of distilled water. The precipitates were centrifuged, washed with methyl alcohol, acetone, ethyl ether, and vacuum dried. The complete O-deacetylation was confirmed by the disappearance of C=O absorption in the infrared spectrogram.

2. 5 Synthesis of N-methylmorpholine-N-oxide monohydrate

The N-methylmorpholine-N-oxide monohydrate (MMNO) was synthesized by reacting methylmorpholine with hydrogen peroxide according to VanRheenen's method[10]. The

MMNO was concentrated in a rotary evaporator under reduced pressure, and MMNO crystal was formed when the solution was stored overnight in a refrigerator. The crystal was then washed with acetone to remove unreacted methylmorpholine, and vacuum dried. The melting point of the crystalline MMNO monohydrate was 72.0°C.

2.6 Limiting viscosity number of the regenerated cellulose in N-methylmorpholine-N-oxide

Viscosities of the seven regenerated fractions were measured in MMNO monohydrate at 80.00±0.04°C. The solutions were prepared by weighing both the regenerated cellulose and MMNO monohydrate; MMNO monohydrate was added to the regenerated cellulose in an Ubbelohode-type viscometer. It was necessary to heat above 72°C in order to get MMNO monohydrate into solution. The concentrations were changed by the addition of MMNO monohydrate into the viscometer. The viscosity measurements were performed in nitrogen atmosphere. The cellulose concentration was estimated based on the density value of MMNO monohydrate, 1.13g cm^{-3} at 80°C.

3. Results and discussion

Table 1 shows the results of the fractionation of the cellulose triacetate in methylene chloride-ethyl alcohol system. Percent ethyl alcohol present at each saturation point is given. As can seen from the ratios, emergence of the precipitate was greatly influenced

Table 1. Methylene chloride-ethyl alcohol fractionation of cellulose triacetate

Fraction	CH_2Cl_2/C_2H_5OH ratio	Weight mg	Dispersity*
I	44.3/55.7	228.9	3.2
II	44.0/56.0	490.2	2.6
III	43.2/56.8	314.6	2.7
IV	41.0/59.0	579.0	1.5
V	38.0/61.8	420.7	1.7
VI	33.9/66.1	215.6	1.4
VII	evaporated	430.6	1.3

* based on the GPC data (standard polystyrene sample)

by small change of solvent mixture, and it is naturally anticipated that an undesirable lower molecular weight CTA would be contaminated in the fraction of higher molecular weight. Therefore, the redissolution of the emerged precipitate by raising the temperature followed by an extremely slow cooling would be effective to minimize the contamination of the lower molecular weight. In spite of this precaution in the precipitation procoss, rather large dispersity values were resulted especially in the highest molecular weight fraction. This is certainly stemmed from the higher initial CTA concentration in which an equilibrium is most difficult to attain.

Before obtaining average molecular weight of each fraction, apparent molecular weight was evaluated from equation (1), and the reciprocals of apparent molecular weight are plot-

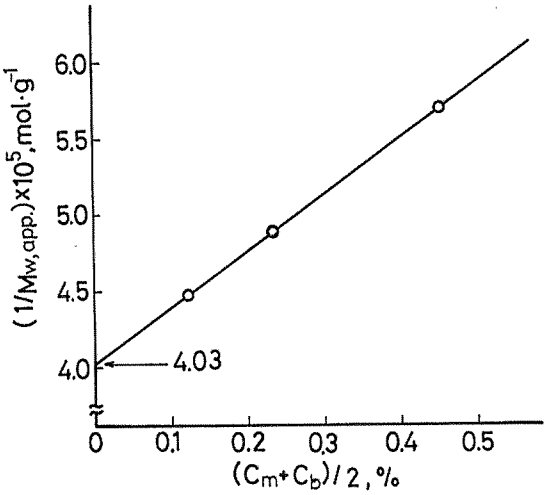

Fig. 1. Plots of $1/\bar{M}_{w\ app}$ against $(C_m+C_b)/2$ for the cellulose triacetate fraction IV in acetone at 25°C.

ted against for various concentrations, $\bar{M}_m$ can be evaluated by extraporating $(C_b+C_m)/2$ to zero using equation (2). Figure 1 shows typical these plots for three different concentrations, 0.1, 0.2 and 0.4%, of the cellulose triacetate fraction IV which were measured in acetone at 25°C.

Table 2. Molecular weights and limiting viscosity numbers of fractionated cellulose

Fraction	$\bar{M}_w\times10^{-4}$, g mol^{-1}		$[\eta]$ ml g^{-1}
	CTA	Reg. Cellulose	
I	5.39	3.07	72.8
II	4.43	2.53	61.7
III	3.64	2.07	55.3
IV	2.48	1.41	46.1
V	1.73	0.99	36.0
VI	1.03	0.59	26.2
VII	0.61	0.35	18.6

Table 2 shows the molecular weight of cellulose fractions based on the sedimentation equilibrium experiments. The molecular weights of the regenerated cellulose were calculated from their degree of substitution, 2.9, assuming that the cellulose acetate would not degrade upon O-deacetylation. This is a fair assumption since the deacetylation was take place in moisture free medium in which new metallic sodium was added each time to methyl alcohol in order to produce fresh 2M sodium methoxide.

In viscosity measurements, both η_{sp}/c and $(\ln\eta_r)/c$ were plotted against the concentrations, and the limiting viscosity numbers were estimated by extraporating the values to concentration zero. The concentration of the cellulose ranged from about 7 to 1.5 and both extraporated values always agreed within a limit of the experimental error. The average

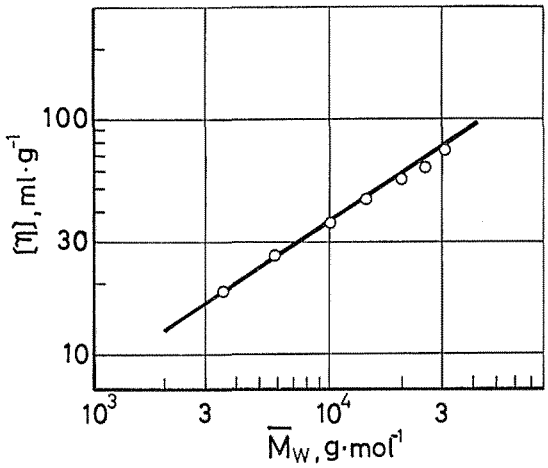

Fig. 2. Limiting viscosity number-weight average molecular weight relationship for cellulose in MMNO at 80°C.

of two values is listed in the right column of Table 2.

When the weight average molecular weights of regenerated cellulose fractions were plotted against the limiting viscosity numbers, both in logarithm scale, the constants in Houwink-Mark-Sakurada's equation can be calculated from the slope and the intercept of the straight line. Figure 2 shows the limiting viscosity number-weight average molecular weight relationship for cellulose in MMNO monohydrate at 80°C., and calculated constants were found to be $K=0.087\pm0.036$ ml g^{-1} and $a=0.66\pm0.04$. These values are given with 95% confidence intervals.

The a value is typical of flexible polymers, and in the range or smaller than those of cellulose triacetate (at 20−25°C)[11]. Considering that cellulose triacetate is less flexible than cellulose, and that the temperature of the viscosity measurement in the present work, 80°C, is much higher than 20-25°C, it is quite reasonable that the cellulose has a smaller a value at 80°C.

The following two questions should be discussed before one takes this relationship legtimate; whether or not MMNO monohydrate is really a nondegrading cellulose solvent, and whether or not it decomposes at high temperature such as 80°C. For the first question we can say MMNO is nondegrading at least in nitrogen atmosphere. In viscosity measurement it usually takes over 24 hours to obtain one limiting viscosity number, and yet we did not see any noticeable viscosity drop due to degradation during the dilution processes. Regarding the possibility of decomposition of MMNO, one can deny with 100% confidence. As MMNO monohydrate melts at 72°C, and anhydrous MMNO at 172°C[12], MMNO monohydrate only loses its hydrating water even it is heated above 172°C. Therefore, within the temperature range we have worked, it is certain that MMNO monohydrate would never be decomposed.

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